1 / VOL. 3, NO. 6
THE CHEMICAL EDUCATOR

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (98) 06271-X

Laboratories and Demonstrations

Recreation of Wöhler's Synthesis of Urea: An Undergraduate Organic Laboratory Exercise

JAMES D. BATCHELOR, EVERETT E. CARPENTER,
GRANT N. HOLDER, CASSANDRA T. EAGLE*
Department of Chemistry
Appalachian State University
Boone, NC 28608
eaglect@appstate.edu

JON FIELDER, AND JARED CUMMINGS
Department of Chemistry
Williams College
Williamstown, MA 01267

The synthesis of urea provides students with experience in both recrystallization and characterization techniques.

An undergraduate laboratory exercise appropriate to the upper-level organic or inorganic course is presented. The objective of the laboratory is to recreate an experiment of historical significance familiar to organic chemistry students while also incorporating modern techniques of spectroscopic characterization and purification.

Introduction

The story is familiar to most organic chemistry students. The compound urea, $(NH_2)_2CO$, isolated from urine by Rouelle in 1773 [1], was the product of Friedrich Wöhler's serendipitous synthesis in 1828, which began as an attempt to synthesize ammonium cyanate. When Wöhler treated silver cyanate with ammonium chloride, he isolated a white, crystalline material with none of the properties of cyanates; another attempt using lead cyanate and ammonium hydroxide lead to uncontaminated white crystals that had organic properties. The white crystals were tested against urea (isolated from urine using potash, chalk, and various acids and bases in the best manner of the day) [2]; the two compounds were identical. Thus, it was discovered that ammonium cyanate had rearranged to form urea.

Most organic chemistry texts point towards this synthesis, as well as Wöhler's previous synthesis of oxalic acid from cyanogen (1824) as the beginning of modern organic chemistry [3]. While this may be an oversimplification, it can be argued that these preparations of organic substances from nonorganic precursors were an unexpected outcome with profound repercussions for the burgeoning science of chemical synthesis. Further, these were the first recorded laboratory syntheses of compounds found in living organisms. The most widely held belief of the day was that "vital" compounds, that is, those which were of animate origin, could only be produced within a lifeform [4]. Thus, if one wanted a sample of urea, reclaiming it from urine was the only way to get it. While Wöhler's work did not destroy vitalism in a single stroke (it exists in some forms to this day), it did, with such pivotal experiments as Kolbe's acetic acid synthesis (1844), begin the accumulation of contraindicative evidence leading to vitalism's eventual rejection [5].

Wöhler did not understand the reaction at the time; investigations since 1828 have shown the mechanism for the conversion of ammonium cyanate to urea to be bimolecular [6], proceeding through dissociation into ammonia and isocyanic acid, followed by recombination and rearrangement to form urea, a more stable product:

$$\mathrm{NH_4NCO} \rightleftharpoons \mathrm{NH_3} + \mathrm{H{-}N{=}C{=}O} \rightleftharpoons \mathrm{(H_2N)_2CO}$$

Further, these studies have indicated that this reaction is not complete in aqueous solutions, and that the bimolecular rate constant is higher in mixtures of water with alcohols than in pure water [7].

This article describes an experiment suitable for sophomore students at which level this important experiment is performed. The exercise gives students a straightforward synthesis that bridges the gap between introductory chemistry and organic chemistry. The product, urea, is obtained in high yield and involves the use of precipitation,

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (98) 06271-X

separation, and recrystallization techniques. Urea lends itself without complication to characterization with infrared spectroscopy, and its purity can be assessed by a melting point determination. The exercise can be completed in two three-hour periods, or with some revisions it can be reduced to one three-hour laboratory period.

In addition, the experiment has the advantage of being pertinent. In many instances students may not appreciate the nuances of the reasoning behind their laboratory assignments; all too often the ubiquitous distillation of benzaldehyde or the like may seem like so much busy work. In contrast, this synthesis is of clear historical importance and, as such, has readily definable and appreciable goals, and its completion is accompanied by a sense of satisfaction. It is also relevant, as urea is the 16th most produced industrial chemical; more than 15 billion pounds per year are produced. Its major use is as the nitrogen source for fertilizers although there are many other applications, including the synthesis of polyurethanes and as a protein substitute for livestock [8].

Experimental

Materials

The reagents used in this experiment can be purchased from most chemical companies. The ordering information from VWR is included herein. All chemicals are Mallinckrodt AR grade except the KBr, which is infrared grade: $Pb(NO_3)_2$ (MK574404), KCNO (MK689003), 2-propanol (MK303219), NH_4OH (MK325610), KBr (MK050002).

Safety Precautions and Waste Considerations

Lead compounds can be hazardous if ingested or inhaled. Ammonia is pungent. Work in an area with adequate ventilation while wearing gloves. Discarded samples of these compounds should be treated as heavy metal waste and disposed of properly.

Measurements

Infrared spectra were recorded on a Nicolet Magna-IR 550 FT-IR infrared spectrometer using a deuterated triglycine sulfate (DTGS) detector. Adequate spectra are obtained from Nujol mulls, KBr pellets, or diffuse reflectance Fourier transform (DRIFT) sampling techniques. Typically, a sample is prepared that is 1–10% urea by mass in Nujol or KBr. The resolution is set at 4 cm^{-1} and 1–4 transients are taken.

Procedure

In the initial reaction, lead(II) cyanate must be prepared according to the equation:

$$\mathrm{Pb(NO_3)_2}(aq) + \mathrm{2KCNO}(aq) \rightarrow \mathrm{Pb(CNO)_2}(s) + \mathrm{2KNO_3}(aq)$$

A volume of 150 mL of 0.010 M lead(II) nitrate and 150 mL of 0.14 M potassium cyanate were poured simultaneously into a 500-mL beaker. The mixture was cooled in an ice bath for 15 min, then filtered under vacuum to remove the precipitate, lead(II) cyanate.

The precipitate was washed several times with distilled cold water and with two 15-mL portions of ethanol. The filtrate was dried in an oven (95 °C) for fifteen minutes, and then cooled in a dessicator.

While cooling was taking place, 200 mL of solvent mixture was prepared by mixing 100 mL of concentrated ammonium hydroxide and 100 mL of 2-propanol.

To prepare urea, 1.00 g of lead(II) cyanate and 60 mL of the solvent mixture were combined in a 100-mL beaker. The reaction mixture was then heated to between 60 °C and 80 °C for 90 min in a fume hood. The volume of the reaction mixture was carefully maintained at 60 mL; solids, which splashed onto the beaker walls, were washed into the reaction mixture using the solvent mixture. The double displacement reaction produced ammonium cyanate, which rearranged to form urea according to:

$$\mathrm{Pb(CNO)_2 + NH_3 + H_2O \rightarrow Pb(OH)_2 + NH_4CNO}$$

followed by:

$$\mathrm{NH_4NCO \rightleftharpoons NH_3 + H{-}N{=}C{=}O \rightleftharpoons (H_2N)_2CO}$$

Purification of urea

The urea was separated from the insoluble lead(II) hydroxide by vacuum filtration. The filtrate was then washed twice with 10 mL of hot water to extract the remaining urea. The supernatant was transferred to a 150-mL beaker and the filtration flask washed with a 10-mL portion of hot water, which was also added to the supernatant. The resulting supernatant and wash solutions were concentrated to less than 20 mL by either heating the mixture on a hotplate in a hood or by using a rotary evaporator. The solution was gravity filtered as necessary to remove any solid materials, and any

THE CHEMICAL EDUCATOR http://journals.springer-ny.com/chedr

S 1430-4171 (98) 06271-X

filtrates were washed with two portions of hot distilled water. All supernatant and wash solutions were then evaporated to dryness by either heating the mixture on a hotplate in a hood or by using a rotary evaporator.

Recrystallization

Five milliliters of ethanol were added to the solid urea and heated to form a solution. This was gravity filtered and the filter paper washed with 10 mL of hot ethanol. The ethanol was evaporated by heating until crystals formed. Crystals of urea were produced in high purity with 80% yield.

Characterization

The purity of urea was assessed by mp determination. The literature mp of urea is 130–133 °C while the experimental value was 129–132 °C[1] suggesting sufficient purity of the student prepared sample. Infrared spectroscopy was also utilized as a characterization method. Urea has distinguishing absorptions, 1680 cm^{-1} ($\nu_{C=O}$), as well as N–H stretches at 3320 and 3420 cm^{-1} (ν_{N-H}). Three sampling preparations (Nujol mull, KBr pellet, and DRIFT) were employed with equal success. Figure 1 shows a comparison of two infrared spectra, one (upper) taken from a student preparation and another (lower) showing the spectrum of Aldrich Gold Label urea. Each sample was prepared identically. Note the high degree of correlation indicating the excellent purity of the student-prepared urea.

Practical aspects of the laboratory

The exercise requires two 3-hour laboratory periods. In the first period, lead(II) cyanate is prepared, and the urea is synthesized and purified. The second period involves further purification, recrystallization, and characterization. The experiment can be completed in less time if the lead(II) cyanate is prepared for the students and if the urea is characterized by only one technique.

Conclusion

This laboratory provides second-semester introductory chemistry students with a springboard into organic synthesis, supplying a facile technique with high yields. The

---

[1] The actual literature value for the melting point of urea according to the CRC handbook is 132.8 °C. The value reported is of stock urea with the melting point determined in the same manner as student preparations.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (98) 06271-X

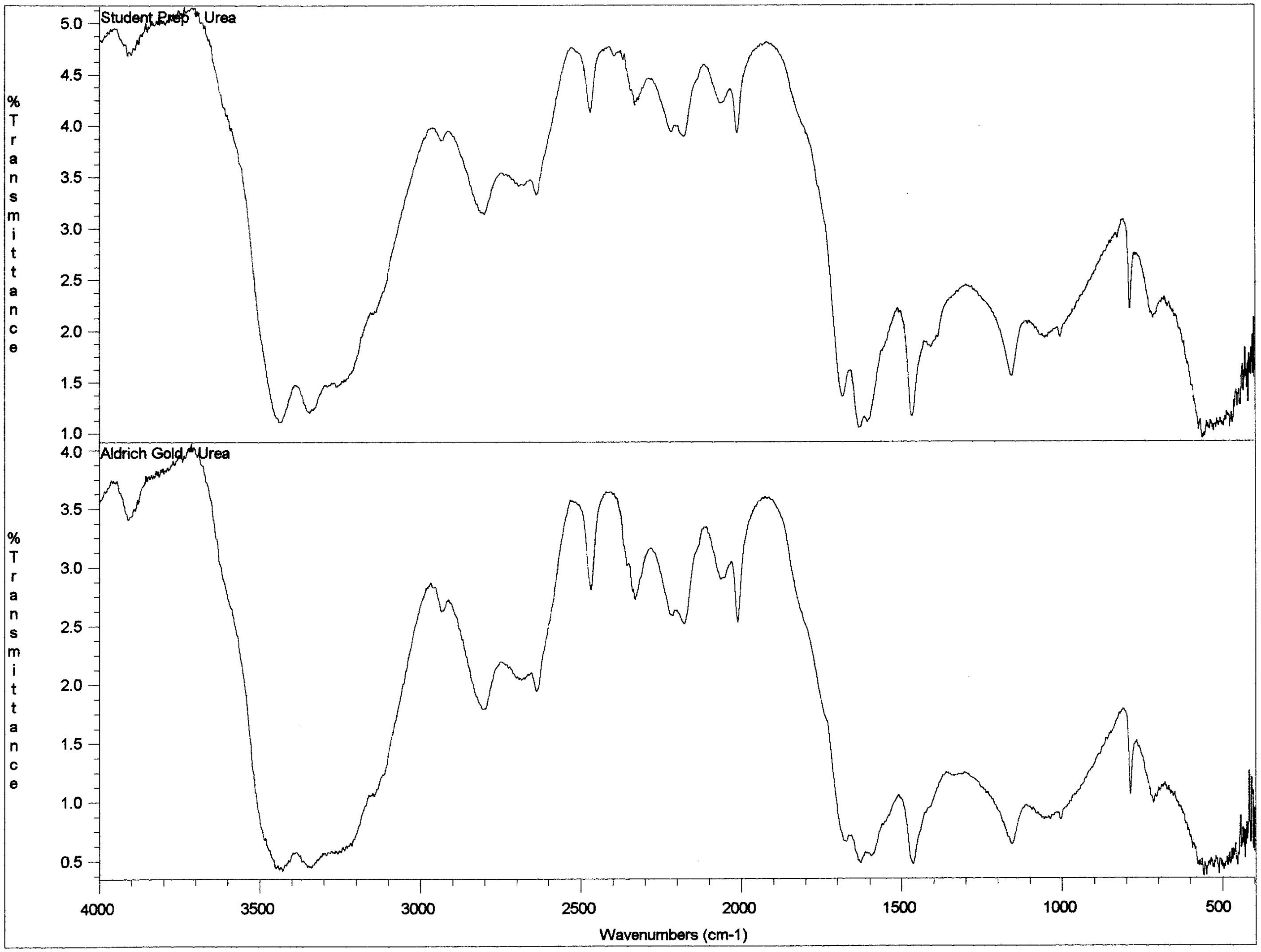

FIGURE 1. FT-IR OF STUDENT PREPARED UREA (UPPER TRACE) AND COMMERCIAL (ALDRICH, 99%) UREA (LOWER TRACE). BOTH SPECTRA WERE TAKEN BY THE DRIFT TECHNIQUE. THE SAMPLE WAS PREPARED USING 10% BY MASS UREA IN KBR. FOUR TRANSIENTS WERE TAKEN EMPLOYING 4 CM^{-1} RESOLUTION.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (98) 06271-X

laboratory also helps students learn how to maximize yields by giving visual clues to areas where product may be lost (urea crystallizes easily with crystals forming on glassware where washing was not efficient). The synthesis of urea provides students with experience in both recrystallization and characterization techniques. The reactions involved in this laboratory demonstrate a variety of topics, including solubility rules and precipitation reactions. The laboratory can be completed in either three or six hours, suitable for either the end of second-semester introductory chemistry or the beginning of first-semester organic chemistry.

ACKNOWLEDGMENT

We thank the Introductory Chemistry classes of Williams College and the Inorganic Chemistry classes of Appalachian State University that tested this experiment.

We thank David G. Farrar for his assistance in the literature review for this project, Joseph Sadighi for useful conversations in the beginning stages of this project, Ann Holder for advice on the proper handling of lead compounds and ordering information for the reagents, and Steve Wyatt for testing the final version of this manuscript in the laboratory.

REFERENCES

1. Adams, R.; Johnson, J. R.; Wilcox, C. F., Jr. *Laboratory Experiments in Organic Chemistry*, 5th ed.; MacMillan Publishing: New York, 1963, p 260.
2. Wöhler, F.; Annalen der Physik und Chemie, **1828**, 12, 253.
3. Wade, L. G., Jr. *Organic Chemistry*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1991; p 1.
4. Birdwhistell, R. K.; *J. Chem. Educ.* **1996**, *73* (9), p 883.
5. *A Source Book In Chemistry, 1400–1900*; Klickstein, H. S.; Leicester, H. M., Eds.; Harvard University Press: Cambridge, MA, 1952; pp 309–312.
6. Walker, J.; *J. Chem. Soc.* **1895**, *67*, 746; Walker, J. *J. Chem. Soc.* **1897**, *71*, 489; Ross, *J. Chem. Soc.*, **1914**, *105*, 690; Werner, *J. Chem. Soc.*, **1912**, *101*, 170; Moelwyn-Hughes, *Chem. Rev.*, **1932**, *10*, 244.
7. Warner, J. C.; Stitt, F. B.; *J. Chem. Soc.*, **1933** (55), 4807.
8. *Chem. Eng. News*, **1994**, *72* (April 12), 12.